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Research Note

Triarylimidazoles as potent antiwear agents: Eco-friendly synthesis and materialistic approach

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Abstract. The load-carrying capacity and wear properties of selected triaryl substituted imidazoles were evaluated using a four-ball test machine. These derivatives show better antiwear performance in comparison to paraffin oil alone, which is confirmed by an Atomic Force Microscope. Thus, these substituted imidazole derivatives can be used as an antiwear agent for steel balls. Triarylimidazoles were synthesized by a one pot three component reaction assisted by recyclable and novel 1-ethyl-3-methylbenzimidazolium iodide $[Embim]^+I^-$ in ecofriendly aqueous condition. This inexpensive, easily synthesized catalyst efficiently catalyzes the condensation of 1,2-diketones, aromatic aldehyde and ammonium acetate. Besides the recycling of the catalyst, the short reaction time, excellent product yield and use of water display both economic and environmental advantages.

1. Introduction

The wear properties of heterocyclic compounds have been reported in recent literature as antiwear and extreme pressure additives, since heterocyclic compounds have compact and stable structures [1,2]. Ren et al. [3] studied the effect of the molecular structure of *N*-containing heterocyclic compounds on their wear property. The five membered heterocyclic compounds are common structural subunits in many polycyclic natural products [4] and various medicinal leads [5]. The *N*-containing heterocyclic compounds, especially imidazoles, have attracted more attention during recent years due to their biological and materialistic performance.

The compounds bearing an imidazole scaffold have shown many pharmacological properties and play an important role in biochemical processes [6a]. The potency and wide applicability of the imidazole pharmacophore can be attributed to its hydrogen bond donor-acceptor capability, as well as its high affinity for metal ions such as Zn, Mg and Fe, which are present in many protein active sites [6b].

Various methods for the synthesis of imidazoles are reported in literature. Generally, 2,4,5-triarylsubstituted imidazoles are synthesized by the three component cyclocondensation of 1,2-diketones with an aldehyde and ammonium acetate [7]. The other methods for synthesis of imidazole include a hetero-cope rearrangement [8], the reaction of 1,2-aminoalcohols in the presence of PCl_5 [9], *N*-(2-oxo) amides with ammonium trifluroacetate [10], diketones, aldehydes, amines and ammonium acetate in the presence of phosphoric acid [11], in ammonium trifluoroacetate [12], and thiazoliumorganocatalyst in acetic acid [13], as well as in H_2SO_4 [14]. In addition to these traditional methods, microwave (MW) assisted synthesis of imidazole from 1,2-diketones, and aldehydes in the presence of different catalysts has been reported recently. These include silicagel [15], silica gel H-Y [16], Al_2O_3 [17], acetic acid [18a,b], in DMF [19], $ZrCl_4$ [20], $NiCl_2.6H_2O$ [21], ionic liquids [22], io-

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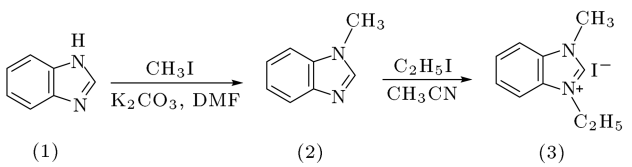
dine [23], sodium bisulphate [24], Ceric Ammonium Nitrate (CAN) [25], PEG-400 [26], sulphanilic acid [27] and *p*-TSA [28].

To address the aforementioned problems, the triarylimidazoles were synthesized by one-pot cyclocondensation of benzil, aromatic aldehyde and ammonium acetate in the presence of 1-ethyl-3-methylbenzimidazolium iodide ([EMIM]+I-) as a novel ionic liquid, and its catalytic activity was checked. It successfully catalyzes the reaction in many organic solvents, such as ethanol, methanol, propanol, t-butanol, and acetonitrile at moderate temperature with very good yield. Encouraged by these results, it was decided to apply this catalyst to an aqueous medium and very positive results were obtained. The most enthusiastic part of this catalyst is its recyclability, as it has a readily soluble nature in water in comparison to any other organic solvents, in less time and with very good yield. The catalyst used in this process is easy to handle, can be recycled, and is eco-friendly in nature, as it works in aqueous media instead of hazardous organic solvents. These synthesized imidazole derivatives were checked for antiwear performance, and as a lubricant additive in liquid paraffin (base oil). They were evaluated using a Seta-Shell four ball lubricant testing machine.

2. Results and discussion

The novel 1-Ethyl-3-methylbenzimidazolium iodide $[Embim]^+I^-$ (3) was synthesized in a two-step reaction. The first step was comprised of N-methylation of benzimidazole using methyl iodide and potassium carbonate as a base, in DMF. This 1-methylbenzimidazole (2) was further alkylated using ethyl iodide in acetonitrile to afford 1-Ethyl-3-methylbenzimidazolium iodide $[Embim]^+I^-$(3) (Scheme 1). The final product (3) was used as a catalyst in the preparation of various triarylsubstitutedimidazoles (7a-p).

It was established from the experiments that 5 mol% of the catalyst was enough to catalyze the synthesis of triarylimidazoles from the condensation of benzil (2m mol), aromatic aldehyde (2m mol) and ammonium acetate (6m mol) in methanol or ethanol at 60°C. So, we decided to apply the same condition in water. This failed, as no trace of the desired product was observed from T.L.C., even after 24 hours continuous reaction. It was then decided to increase the temperature to 90°C, but still no product was observed from T.L.C. Then, the temperature was increased to 100°C and, after 10 minutes, a spot of the desired product was visualized on T.L.C. The reaction was continued for 2 hours leading to a poor yield (24%). The amount of catalyst was then increased up to 20 mol%, leading to an increase in product yield to 32%. After that, the temperature of the reaction was increased up to 105°C and 36% yield was obtained within 30 minutes. Excited by this result, we decided to study the effect of temperature on this condensation reaction. It was observed that by increasing the temperature to 115°C, the reaction was completed within 10 minutes, giving a yield of 92%. We further increased the temperature up to 125°C, but shortened the time period. The details of the results obtained are summarized in Table 1.



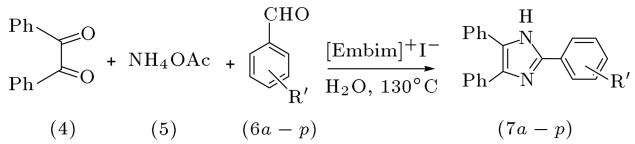
Scheme 1. Synthesis of 1-ethyl-3-methylbenzimidazolium iodide $[Embim]^+I^-$.

We also evaluated the amount of catalyst required for this synthesis in water and it was found that in 5 mol%, 10 mol%, and 15 mol% of the catalyst at 115°C, we obtained 46%, 58% and 74% yields, respectively. The maximum yield of 92% was obtained when the reaction was loaded with 20 mol% of the catalyst. A further increase in catalyst does not affect the yield. Thus, it was established that 20 mol% of the catalyst at 115°C was the best condition for one-pot cyclocondensation of benzil (2m mol) and ammonium acetate (6m mol) in water (Scheme 2).

We next examine the reaction condition to a wide variety of aromatic aldehydes with various substituents to establish the catalytic importance of 1-ethyl-3-methylbenzimidazolium iodide for this cyclocondensation reaction in water. A wide range of

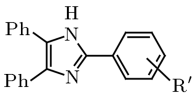
Table 1. One-pot condensation of benzil, benzaldehyde and ammonium acetate at different temperature and different catalyst%.

Entry	Catalyst (%)	Temp. (°C)	Time	Yield (%)
1	5	60	48 h	0
2	5	90	48 h	0
3	5	100	4h	24
4	20	100	4h	32
5	20	105	30 min	36
6	20	110	15 min	62
7	5	115	10 min	46
8	10	115	10 min	58
9	15	115	10 min	74
10	20	115	10 min	92
11	25	115	10 min	90
12	30	115	10 min	90
13	20	120	8 min	92
14	20	125	6 min	92



Scheme 2. General scheme for synthesis of triarylsubstitutedimidazoles using $[Embim]^+I^-$ as catalyst.

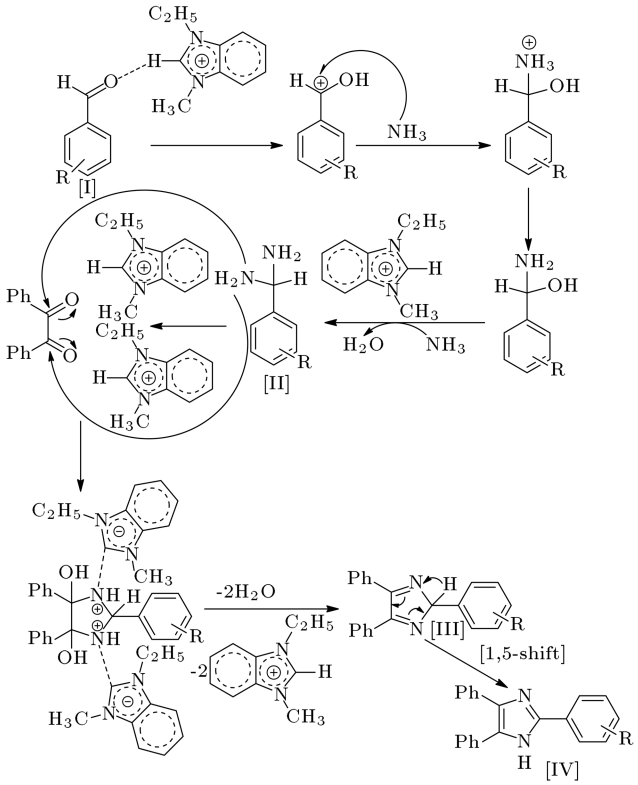
Table 2. Yields (%) and reaction time of variously substituted triarylimidazoles.



S. No.	R′	Time (min.)	Yield (%)	M.P. (°C)
7a	H	10	92	268-272
7b	3-NO_2	4	90	195-198
7c	2-Cl	5	91	189-192
7d	4-OCH_3	10	93	220-223
7e	3-OCH_3	10	90	272-275
7f	2-OCH_3	8	88	210-212
7g	4-OC_2H_5	10	88	223-226
7h	3-OC_2H_5	10	91	250-255
7i	2-OC_2H_5	8	92	165-169
7j	4-OCH_2Ph	8	91	226-230
7k	3-OCH_2Ph	10	89	134-136
7l	2-OCH_2Ph	10	89	145-149
7m	3,4,5-$(OCH_3)_3$	10	92	249-254
7n	4-OH	8	91	244-246
7o	3-OH	5	90	254-258
7p	2-OH	10	85	203-207

ortho-, meta- and para- substituted aromatic aldehydes underwent condensation with benzil and ammonium acetate to afford 2,4,5-triarylsubstituted imidazoles ($7a - p$) in very good yields (Scheme 2). In all cases, we observed almost the same performance of the catalyst cyclocondensation in giving the desired product (Table 2).

The workup of this reaction was very simple, giving the pure product without application of any chromatographic procedures. The completion of the reaction was monitored through T.L.C. and also marked by separation of the solid imidazole product. Since no side reaction occurred and the product was almost pure, after the completion of the reaction, a workup was conducted by simply filtering the reaction mixture. The residue was washed with water, dried and recrystalised from ethyl acetate to get pure imidazoles ($7a - p$). All the synthesized 2,4,5-triaryl substitutedimidazoles have been characterized on the basis of elemental analysis and spectral studies.



Scheme 3. Probable mechanism for the synthesis of triarylimidazoles.

In order to explore the recycling ability of the catalyst, we preserved the filtrate water layer showing the spot of catalyst in T.L.C., as it is readily soluble in water. We used this filtrate to further the condensation reaction, and imidazole formation occured five times successfully, without any complications. This recycling ability and easy handling of the catalyst also makes the process more convenient and the use of water as a solvent, instead of harmful organic solvents, makes the process easy and eco-friendly.

The probable mechanism of this condensation reaction, i.e. formation of triaryl substitutedimidazoles by the catalytic activity of $[Embim]^+I^-$, is shown in Scheme 3. First, the $[Embim]^+I^-$ promotes the splitting of ammonium acetate to generate the ammonia required for the initial condensation. Also, it is known that >N-H hydrogen of benzimidazoliumcation is acidic in nature. This acidic character of >N-H hydrogen enables the benzimidazoliumcation to bond with the carbonyl oxygens of 1,2-diketones, increasing its reactivity. Further, the benzimidazoliumcation facilitates the formation of diamine intermediate (II), which, under mild acid catalysis of benzimidazoliumcation, condenses with carbonyl carbons of the 1,2-diketone. This got dehydrated to afford imino (III), which rearranges via a [1,5] sigmatropic shift to the required 2,4,5-triarylimidazoles (IV).

Table 3. Wear scar diameter of 1.0 wt% imidazole derivatives in liquid paraffin oil at 392 N for 60 minutes test duration.

Additive	Wear scar diameter (mm)
Liquid paraffin	0.699
2-(3-nitrophenyl)-4,5-diphenyl-1*H*-imidazole	0.600
2-(4-methoxyphenyl)-4,5-diphenyl-1*H*-imidazole	0.611
2-(3-ethoxyphenyl)-4,5-diphenyl-1*H*-imidazole	0.632
2-(4,5-diphenyl-1*H*-imidazol-2-yl)-phenol	0.648
4-(4,5-diphenyl-1*H*-imidazol-2-yl)-phenol	0.622
4,5-diphenyl-2-(3,4,5-trimethoxyphenyl)-4,5-diphenyl-1*H*-imidazole	0.629

3. Tribological performance of synthesized additives

The surface morphology of the wear scars on the steel balls is observed after antiwear testing at load 392 N for 60 minutes test duration in paraffin oil. These substituted imidazole derivatives show better antiwear properties in comparison to liquid paraffin (Table 3).

The wear on the steel ball was studied by Atomic Force Microscopy in the presence of the most effective additive **imidazoles**. All the roughness parameters, summarized in Table 4, are obtained through processing the AFM images by digital instrument software. Figure 1(a) and (b) illustrate two and three dimensional (deflection) images of the wear scar in paraffin oil and in the presence of additive **imidazole**, respectively. As apparent from the data and the figures, the roughness has fairly reduced in the presence of the additives (Figure 1). The reduction in surface roughness may be attributed to the tribofilm formed under test conditions by the adsorbed additive. Moreover, there is a drastic reduction in surface roughness.

Table 4. Surface roughness parameters obtained from digital processing software of nanosurf-basic Scan 2 at 392 *N* and 60 minutes test duration.

Liquid paraffin		**Imidazole**	
Area roughness		**Area roughness**	
Area	2.496 nm^2	Area	2.496 nm^2
Sa	256.93 nm	Sa	17.916 nm
Sq	330.52 nm	Sq	23.831 nm
Sy	3.2386 μm	Sy	319.22 nm
Sp	2096.4 nm	Sp	151.83 nm
Sv	-1142.2 nm	Sv	-167.39 nm
Sm	141.62 pm	Sm	303.91 pm
Line roughness		**Line roughness**	
Ra	197.51 nm	Ra	389.07 nm
Rq	263.98 nm	Rq	466.51 nm
Ry	1391.5 nm	Ry	1678.7 nm
Rp	871.92 nm	Rp	522.39 nm
Rv	-519.59 nm	Rv	-1156.3 nm
Rm	147.46 pm	Rm	111.66 pm

4. Experimental

4.1. General

All reagents were commercial and purchased from Merck, Aldrich and were used as received. All the reactions were monitored by thin layer chromatography over **silica Gel G TLC** plates. The melting points were recorded on electrically heated instruments and are uncorrected. All ^{1}H and ^{13}CNMR spectra were recorded on a **JEOLAL300 FT-NMR** spectrometer using tetramethylsilane as the internal reference, and chemical shift values are expressed in δ ppm units. Mass spectra of compounds were taken with **JEOLSX 102/Da-600** mass spectrometer. Analysis was performed on an Exter Analytical Inc. "**Model CE-440 CHN Analyzer**" instrument.

4.2. Preparation of 1-methylbenzimidazole (2)

1 eq. of benzimidazole (1), 1.5 eq. of methyliodide and 1 eq. of potassium carbonate were stirred in DMF at room temperature for 15 hrs. Completion of the reaction was monitored through T.L.C. DMF was removed through rotavapour and the product was extracted using chloroform and water. The organic layer was dried over sodium sulphate, and the solvent was evaporated through the rotavapour and recrystallized using ethyl acetate and hexane. The product was confirmed through spectral analysis: ^{1}H NMR (300MHz, $CDCl_3$): δ 3.70 (s, 3H, -NCH_3), 7.68-7.76 (m, 4H, Ar-H), 9.66 (s, ^{1}H, N-CH-N); ^{13}CNMR (75MHz, $CDCl_3$): δ 30.8, 109.2, 120.0, 121.9, 122.7, 134.3, 143.4; FABMS: m/z 133 (M+1); Elemental analysis for $C_8H_8N_2$: Calcd: C, 72.73%; H, 6.06%; N, 21.21%; Found: C, 72.75%; H, 6.17%; N, 21.25%.

4.3. Preparation of 1-ethyl-3-methylbenzimidazolium iodide [Embim]$^+I^-$ (3)

To a solution of compound (2) in acetonitrile, 1.5 eq. ethyl iodide was added slowly maintaining the temperature at 0°C. After the addition, it was stirred at room temperature for about 1 hour to get a clear

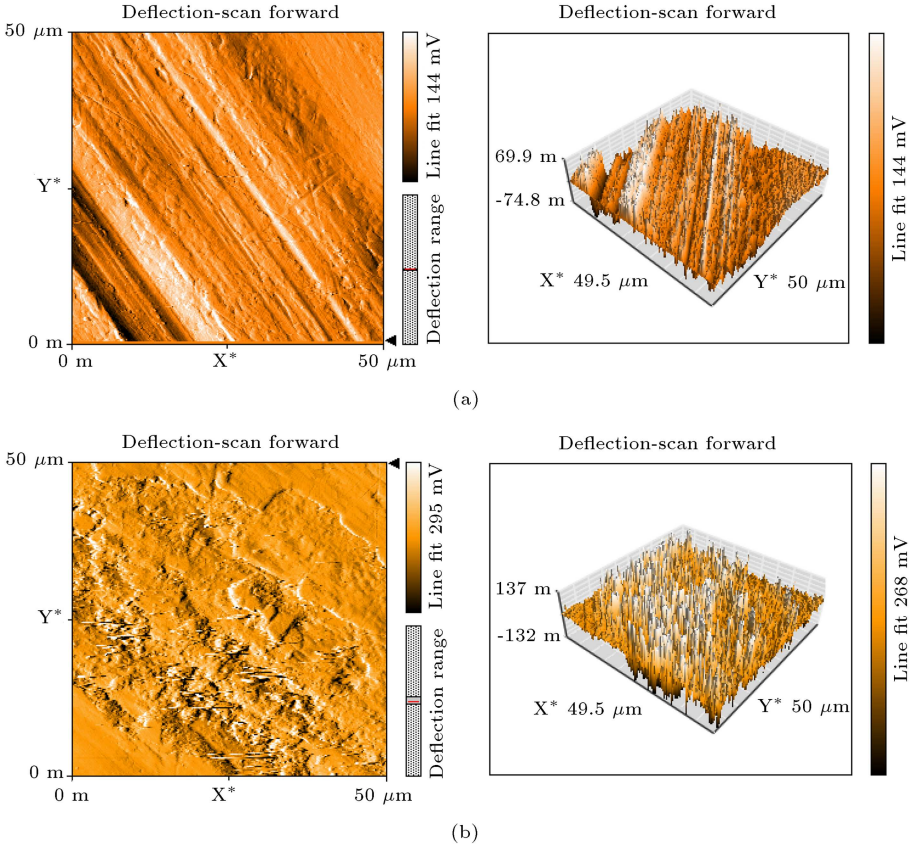


Figure 1. Two dimensional and three dimensional AFM images in (a) paraffin oil, and in (b) the presence of imidazole additives at 392 N load for 60 minutes test duration.

solution. Then, it was stirred at 70°C for 14 hours. Completion of the reaction was monitored through T.L.C. Subsequently, the solvent was evaporated and the product was recrystallized via ethyl acetate and hexane. The product was confirmed through spectral analysis: ^{1}HNMR (300MHz, $CDCl_3$): δ 1.76 - 1.81 (t, 3H, -CH_2CH_3), 4.31 (s, 3H, -NCH_3), 4.62 - 4.69 (q, 2H, -CH_2CH_3), 7.68 - 7.76 (m, 4H, Ar-H), 11.06 (S, 1H, N-CH-N); ^{13}CNMR (75MHz, $CDCl_3$): δ 14.5, 34.1, 42.8, 112.9,113.0, 127.1, 127.1, 130.6, 131.7, 141.2; FAB MS: m/z 289 (M+1); Elemental analysis for $C_{10}H_{13}N_2I$: Calcd: C, 41.66%; H, 4.51%; N, 9.72%; Found: C, 41.5%; H, 4.6%; N, 9.92%.

4.4. General procedure for synthesis of triarylsubstitutedimidazoles (7a – n)

Benzil (2 mmol), aromatic aldehyde (2 mmol), ammonium acetate (2 mmol) and 1-Ethyl-3-methylbenzimidazolium iodide $[Embim]^+I^-$ (20 mol%) were stirred at a temperature of about 115 C in a minimum amount of water (≈10ml). The completion of the reaction was monitored through T.L.C and the duration of the reaction is given in Table 1. After completion of reaction, the reaction mixture was filtered, washed with water, dried and recrystallised through ethyl acetate to get an almost pure product. The structure of the produced 2,4,5-triaryl substituted imidazole was established through spectral analysis (^{1}H NMR,^{13}CNMR and mass spectroscopy).

Synthesis of (7a): R = H. M.P. 268-272°C; Yield: 0.54 g (92%); ^{1}H NMR (300 MHz, DMSO): δ 7.22-8.09 (m, 15H, Ar-H), 12.69 (s, 1H, NH); ^{13}CNMR (75 MHz, DMSO): δ 125.2, 126.5, 127.2, 127.4, 128.0, 128.2, 128.7, 129.6, 130.5, 131.12, 132.3, 135.4, 137.2, 145.6; FAB MS: m/z 297 (M+1); Elemental analysis for $C_{21}H_{16}N_2$: Calcd: C, 85.11%; H, 5.44%; N, 9.45%; Found: C, 85%; H, 5.28%; N, 9.35%.

Synthesis of 2-(3-nitrophenyl)-4,5-diphenyl-1H-imidazole (7b): R = 3-NO_2. M.P. 195-198°C; Yield: 0.65 g (95%); ^{1}H NMR (300 MHz, DMSO): δ 7.41-8.97 (m, 14H, Ar-H), 13.15 (s, 1H, NH); ^{13}CNMR (75 MHz, DMSO): δ 119.5, 122.7, 127.9,128.6, 130.5, 131.2, 131.9, 143.5, 148.4; FAB MS: m/z 342 (M+1); Elemental analysis for $C_{21}H_{15}N_3O_2$: Calcd: C, 73.88%, H, 4.43%; N, 12.31%; Found: C, 73.7%; H, 4.5%; N, 12.22%.

Synthesis of 2-(2-chlorophenyl)-4,5-diphenyl-1H-imidazole (7c): R = 2-Cl. M.P.189-192°C;

Yield: 0.60 g (91%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26-8.48 (m, 14H, Ar-H), 10.23 (s, 1H, -NH); ^{13}CNMR (75 MHz, $CDCl_3$): δ 127.4, 128.8, 130.1, 130.4, 130.5, 131.7, 131.8, 143.6; FAB MS: m/z 331 (M+1); Elemental analysis for $C_{21}H_{15}N_2Cl$: Calcd: C, 76.24%, H, 4.54%; N, 8.48%; Found: C, 76.5%; H, 4.6%; N, 8.5%.

Synthesis of 2-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazole (7d): R = 4-OCH_3. M.P.220-223°C; Yield: 0.60 g (93%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.86 (s, 3H, OCH_3), 6.97-7.86 (m, 14H, Ar-H), 9.33 (s, 1H, -NH); ^{13}CNMR (75 MHz, $CDCl_3$,): δ 55.2, 114.1, 123.0, 126.8, 127.1, 127.7, 128.4, 128.7, 129.5, 129.6, 132.3, 133.2, 135.6, 145.7, 159.5; FAB MS: m/z 327 (M+1); Elemental analysis for $C_{22}H_{18}N_2O$: Calcd: C, 80.98%; H, 5.52%; N, 8.59%; Found: C, 81.1%; H, 5.28%; N, 8.39%.

Synthesis of 2-(3-methoxyphenyl)-4,5-diphenyl-1H-imidazole (7e): R = 3-OCH_3. M.P. 272-275°C; Yield: 0.58 g (90%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.89 (s,3H, -OCH_3), 6.93-7.57 (m, 14H, Ar-H), 9.33 (s, 1H, NH); ^{13}CNMR (75 MHz, $CDCl_3$): δ 55.3, 110.3, 114.3, 117.7, 126.5, 127.2, 128.3, 128.6, 130.0, 131.1, 131.7, 135.1, 137.2, 145.5, 159.6; FAB MS: m/z 327 (M+1); Elemental analysis for $C_{22}H_{18}N_2O$: Calcd: C, 80.98%; H, 5.52%; N, 8.59%; Found: C, 80.8%; H, 5.8%; N, 8.35%.

Synthesis of 2-(2-methoxyphenyl)-4,5-diphenyl-1H-imidazole (7f): R = 2-OCH_3 . M.P. 210-212°C; Yield: 0.57 g (88%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.04 (s, 3H, -OCH_3), 7.02-8.49 (m,14H, Ar-H), 10.48 (s, 1H, NH); ^{13}CNMR (75 MHz, $CDCl_3$): δ 55.6, 111.5, 118.9, 120.6,126.4, 127.1, 127.6, 128.2, 128.9, 129.8, 131.2, 135.3, 136.4, 143.2, 156.0; FAB MS: m/z 327 (M+1); Elemental analysis for $C_{22}H_{18}N_2O$: Calcd: C, 80.98%; H, 5.52%; N, 8.59%; Found: C, 81%; H, 5.3%; N, 8.4%.

Synthesis of 2-(4-ethoxyphenyl)-4,5-diphenyl-1H-imidazole (7g): R = 4-OC_2H_5. M.P.223-226°C; Yield: 0.60 g (88%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42-1.46 (t, 3H, -OCH_2CH_3), 4.04-4.15 (q, 2H, -OCH_2CH_3), 6.94-7.83 (m, 14H, Ar-H); 9.28 (s, 1H, NH); ^{13}CNMR (75 MHz, $CDCl_3$): δ 14.6, 63.1, 114.5, 123.0, 126.4, 126.7, 127.0, 127.6, 128.1, 128.3, 128.6, 131.2, 135.3, 136.7, 145.6, 158.7; FAB MS: m/z 341 (M+1); Elemental analysis for $C_{23}H_{20}N_2O$: Calcd: C, 81.17%; H, 5.88%; N, 8.24%; Found: C, 81%; H, 5.58%; N; 8.35%.

Synthesis of 2-(3-ethoxyphenyl)-4,5-diphenyl-1H-imidazole (7h): R = 3-OC_2H_5. M.P.250-255°C; Yield: 0.61 g (91%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.41-1.46 (t, 3H, -OCH_2CH_3), 4.08-4.15 (q, 2H, -OCH_2CH_3), 6.91-7.56 (m, 14H, Ar-H), 9.31 (s, 1H); ^{13}CNMR (75MHz, $CDCl_3$): δ 14.7, 63.2, 110.8, 114.7, 117.6, 127.2, 128.4, 129.9, 131.6, 145.5, 158.9; FAB MS: m/z 341 (M+1); Elemental analysis for $C_{23}H_{20}N_2O$: Calcd: C, 81.17%; H, 5.88%; N, 8.24%; Found: C, 81.3%; H, 5.9%; N, 8.3%.

Synthesis of 2-(2-ethoxyphenyl)-4,5-diphenyl-1H-imidazole (7i): R = 2-OC_2H_5. M.P.165-169°C; Yield: 0.62 g (92%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.59-1.63 (t, 3H, -OCH_2CH_3), 4.25-4.32 (q, 2H, -OCH_2CH_3), 6.99-8.49 (m, 14H, Ar-H), 10.68 (s, 1H); ^{13}CNMR (75MHz, $CDCl_3$): δ 64.3, 112.0,118.1, 121.5, 1267.1, 127.4, 127.5, 128.4, 128.6, 129.4, 144.2,155.1; FAB MS: m/z 341 (M+1); Elemental analysis for $C_{23}H_{20}N_2O$: Calcd: C, 81.17%; H, 5.88%; N, 8.24%; Found: C, 81.45%; H, 5.96%; N, 8.16%.

Synthesis of 2-(4-benzyloxyphenyl)-4,5-diphenyl -1H-imidazole (7j): R = 4-OCH_2Ph. M.P.226-230°C; Yield: 0.73 g (91%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.12 (s, 2H, -OCH_2Ph), 7.04-7.86 (m, 19H, Ar-H), 9.17 (s, 1H, NH); ^{13}CNMR (75MHz, $CDCl_3$): δ 69.3, 115.0, 123.4, 126.5, 127.1, 127.8, 127.9, 128.2, 128.4, 128.6, 131.2, 135.3, 136.8, 136.9, 145.6, 158.6; FAB MS: m/z 403 (M+1); Elemental analysis for $C_{28}H_{22}N_2O$: Calcd: C, 83.58%, H, 5.47%; N, 6.97%; Found: C, 83.84%; H, 5.28%; N, 7.1%.

Synthesis of 2-(3-benzyloxyphenyl)-4,5-diphenyl -1H-imidazole (7k): R = 3-OCH_2Ph. M.P.134-136°C; Yield: 0.75 g (94%); ^{1}H NMR (300 MHz, DMSO): δ 5.15 (s, 2H, -OCH_2Ph), 7.23-7.75 (m, 19H, Ar-H), 12.65 (s, 1H, NH); ^{13}CNMR (75 MHz, DMSO): δ 69.4, 111.4, 115.0, 117.9, 119.8, 121.9, 127.8, 128.0, 128.6, 129.9, 131.7, 132.3, 136.9, 137.1, 145.4, 158.8, 167.2; FAB MS: m/z 403 (M+1); Elemental analysis for $C_{28}H_{22}N_2O$: Calcd: C, 83.58%; H, 5.47%; N, 6.97%; Found: C, 83.3%; H, 5.6; N, 6.69%.

Synthesis of 2-(2-benzyloxyphenyl)-4,5-diphenyl -1H-imidazole (7l): R = 2-OCH_2Ph. M.P.145-149°C; Yield: 0.71 g (89%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.22 (s, 2H, -OCH_2Ph), 7.05-8.51 (m, 19H, Ar-H), 10.51 (s, 1H, NH); ^{13}CNMR (75 MHz, $CDCl_3$): δ 69.9, 113.1, 119.1, 121.0, 126.6, 127.2, 127.6, 128.0, 128.5, 128.7 129.8, 130.9, 135.2, 136.5, 143.3, 155.2; FAB MS: m/z 403 (M+1); Elemental analysis for $C_{28}H_{22}N_2O$: Calcd: C, 83.58%; H, 5.47%; N, 6.97%; Found: C, 83.29%; H, 5.48%; N, 7.05%.

Synthesis of 4,5-diphenyl-2-(3,4,5-trimethoxy phenyl)-4,5-diphenyl-1H-imidazole (7m): R =

3,4,5-(OCH_3)$_3$. M.P.249-254°C; Yield: 0.65 g (92%); ^{1}H NMR (300 MHz, DMSO): δ 3.70 (s, 3H, -OCH_3), 3.86 (s, 6H, -OCH_3, -OCH_3), 7.20-7.55 (m, 12H, Ar-H), 12.60 (s, 1H, NH); ^{13}CNMR (DMSO, 75MHz): (δ) 56.0, 59.8, 60.2, 102.6,125.9, 126.5, 127.1, 127.9, 128.1, 128.6, 131.2, 135.1, 137.0, 137.7, 145.5, 153.2; FAB MS: m/z 386 (M+1); Elemental analysis for $C_{24}H_{22}N_2O_3$: Calcd: C, 74.61%; H, 5.70%; N, 7.25%; Found: C, 74.72%; H, 5.78%; N, 7.53%.

Synthesis of 4-(4,5-diphenyl-1H-imidazol-2-yl)-phenol (7n): R = 4-OH. M.P.244-246°C; Yield: 0.58 g (91%); ^{1}H NMR (300 MHz, DMSO): δ 6.82-8.31 (m, 14H, Ar-H), 9.70 (s, 1H, -OH), 12.39 (s, 1H, -NH); ^{13}CNMR (75MHz, DMSO): δ 115.5, 121.7, 127.0, 128.3, 146.2, 157.8; FAB MS: m/z 313 (M+1); Elemental analysis for $C_{21}H_{16}N_2O$: Calcd: C, 80.77%; H, 5.13%; N, 8.97%; Found: C, 80.85%; H, 5.28%; N, 9.15%.

Synthesis of 3-(4,5-diphenyl-1H-imidazol-2-yl)-phenol (7o): R = 3-OH. M.P.254-258°C; Yield: 0.56 g (90%); ^{1}H NMR (300 MHz, DMSO): δ 6.75-7.501 (m, 14H, Ar-H), 9.55 (s, 1H, -OH), 12.60 (s, 1H, -NH); ^{13}CNMR (75 MHz, DMSO): δ 112.2, 115.5, 126.5, 127.1, 127.7, 128.5, 128.6, 129.8, 131.1, 131.7, 135.3, 137.1, 145.7, 157.7; FAB MS: m/z 313 (M+1); Elemental analysis for $C_{21}H_{16}N_2O$: Calcd: C, 80.77%; H, 5.13%; N, 8.97%; Found: C, 80.96%; H, 5.38%; N, 9.2%.

Synthesis of 2-(4,5-diphenyl-1H-imidazol-2-yl)-phenol (7p): R = 2-OH. M.P.203-207°C; Yield: 0.55 g (85%); ^{1}H NMR (300 MHz, DMSO): δ 6.79 - 8.64 (m, 14H, Ar-H), 5.95 (s, 1H, -OH), 10.05 (s,1H, -NH); ^{13}CNMR (75 MHz, DMSO): δ 115.3, 118.9, 127.0, 127.6 128.2, 128.5, 129.1, 131.3, 134.6, 155.1, 165.3; FAB MS: m/z 313 (M+1); Elemental analysis for $C_{21}H_{16}N_2O$: Calcd: C, 80.77%; H, 5.13%; N, 8.97%; Found: C, 81.02%; H, 5.32%; N, 9.1%.

5. Conclusions

In conclusion, we have demonstrated that the tribological properties of all the above mentioned synthesized imidazole derivatives exhibit better wear reducing properties than the base oil alone, which is synthesized using a novel, recyclable, and easily handled 1-ethyl-3-methylbenzimidazolium iodide catalyst in an aqueous medium. The process gives rise to excellent yields of 2,4,5-triarylimidazoles in short reaction time (~10 minutes). Thus, this new methodology, using the benzimidazolium ion as the catalyst and water as the medium, is a noteworthy procedure for manufacturing imidazoles in a short time with good yields.

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